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ALGEBRAIC APPROACH TO THE VIBRATIONAL EXCITATIONS IN METHANE

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Abstract

We present a description of the vibrational excitations of methane by means of an algebraic analysis of a model of coupled anharmonic oscillators.

1 Introduction

Consider an AB_4 -like tetrahedral molecule and suppose we are interested in describing its vibrational degrees of freedom. This can be accomplished either in the framework of an integro-differential scheme or by means of an algebraic approach. The former constitutes the traditional method, which consists in parametrizing the Hamiltonian in terms of internal coordinates [1], where the potential is modeled in terms of force field constants that can be obtained from theoretical calculations or from fits to spectroscopic data [2]. On the other hand, the algebraic approach represents an alternative to the traditional methods based on the use of Lie algebras to represent the interactions [3]. The algebra used to describe the vibrational degrees of freedom is not unique. Michelot and Leroy, for example, use a unitary group $U(n)$ as the dynamical group of the system with $n - 1$ vibrational degrees of freedom [4], while Iachello and Oss introduce an $SU(2)$ algebra for each atomic degree of freedom [5]. In this work we carry out a complete description of the vibrational excitations of tetrahedral molecules by assigning a $U(2)$ algebra to each interatomic potential.

2 Algebraic Model

The model is based on the isomorphism of the $U(2)$ algebra with a one-dimensional Morse oscillator, whose eigenstates may be put into a one to one correspondence with a set of $U(2) \supset O(2)$ states, characterized by the quantum numbers $[[N], m >$, as long as the value of m is restricted to be non-negative. In this space the Morse Hamiltonian takes the simple form $\hat{H} =$

$A\hat{C}_{2O(2)}$, where A and N are related to the Morse potential parameters and $\hat{C}_{2O(2)}$ corresponds to the square of the $O(2)$ invariant operator [3].

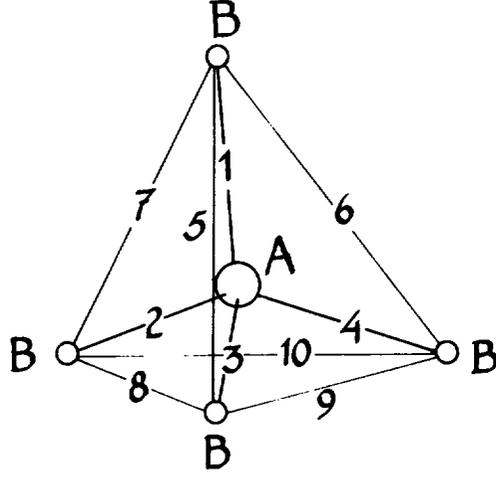


FIG. 1. Assignment of the $U^i(2)$ algebras to tetrahedral molecules.

For the description of a tetrahedral molecule we assign a $U^i(2)$ algebra to each interaction present, as shown in Fig. 1. The first four algebras have been chosen to correspond to the $A-B$ interactions, while the other six represent the $B-B$ couplings. The molecular dynamical group is then given by the product $U^1(2) \times \dots \times U^{10}(2)$, and the most general Hamiltonian, up to two body interactions, conserving the total number of quanta and invariant under the tetrahedral group T_d , can be written as

$$\hat{\mathcal{H}} = \hat{\mathcal{H}}^S + \hat{\mathcal{H}}^B + \hat{V}^{S-B} . \quad (1)$$

The term $\hat{\mathcal{H}}^S$ describes the stretching degrees of freedom and has the form

$$\hat{\mathcal{H}}^S = A_1 \sum_{i=1}^4 \hat{C}_{2O^i(2)} + B_{12} \sum_{i=1}^3 \sum_{j=i+1}^4 C_{2O^{ij}(2)} + \lambda_{12} \sum_{i=1}^3 \sum_{j=i+1}^4 \hat{\mathcal{M}}_{ij} ,$$

while $\hat{\mathcal{H}}^B$ is the bending contribution, given by

$$\begin{aligned} \hat{\mathcal{H}}^B = & A_5 \sum_{i=5}^{10} \hat{C}_{O^i(2)} + B_{5,6} \left\{ \sum_{j=6}^9 \sum_{i=5,10} \hat{C}_{2O^{ij}(2)} + \sum_{j=7,9} \sum_{i=6,8} \hat{C}_{2O^{ij}(2)} \right\} \\ & + B_{5,10} \left\{ \hat{C}_{2O^{5,10}(2)} + \hat{C}_{2O^{6,8}(2)} + \hat{C}_{2O^{7,9}(2)} \right\} \\ & + \lambda_{5,6} \left\{ \sum_{j=6}^9 \sum_{i=5,10} \hat{\mathcal{M}}_{ij} + \sum_{j=7,9} \sum_{i=6,8} \hat{\mathcal{M}}_{ij} \right\} \\ & + \lambda_{5,10} \left\{ \hat{\mathcal{M}}_{5,10} + \hat{\mathcal{M}}_{6,8} + \hat{\mathcal{M}}_{7,9} \right\} . \end{aligned}$$

The last operator, $\hat{V}^{\hat{C}-B}$, represents the stretching-bending interactions, which will be neglected as a first approximation. In these expressions $\hat{C}_{2O^{ij}(2)}$ corresponds to the $O^{ij}(2)$ Casimir invariant, while \hat{M}_{ij} is the Majorana operator, which is related to the $U^{ij}(2)$ Casimir operator [3].

The simplest basis to diagonalize the Hamiltonian is the one associated to the local-mode chain [3]

$$\begin{array}{ccccccccccc}
 U^{(1)}(2) \times \dots \times U^{(4)}(2) \times U^{(5)}(2) \times \dots \times U^{(10)}(2) & \supset & O^{(1)}(2) \times \dots \times O^{(10)}(2) & \supset & O(2) \\
 \downarrow & & \downarrow \\
 [[N_1] , \dots [N_1] & & [N_2] , \dots , & & [N_2] & & v_1 , \dots , & & v_{10}; & & V > ,
 \end{array} \quad (2)$$

where below each group we have indicated the quantum numbers characterizing the eigenvalue of the corresponding invariant operator. The two boson numbers N_1 and N_2 , are related to the two sets of physical modes (stretching and bending). The quantum numbers v_i correspond to the number of phonons in each oscillator ($v_i = \frac{N_i}{2} - m_i$), while $V = \sum_{i=1}^{10} v_i$.

A simple analysis of an AB_4 tetrahedral molecule [6] shows that it presents 9 vibrational degrees of freedom, four of them corresponding to the fundamental stretching modes ($A_1 \oplus F_2$) and the other five to the fundamental bending modes ($E \oplus F_2$). Comparing this result with the local basis (2), we deduce that an unphysical bending mode is present in the algebraic formalism. We thus proceed to eliminate this spurious state both from the Hamiltonian and the basis.

To accomplish this goal we first transform, for the one phonon case, the local basis to a normal one, which carries the irreducible representations (irreps) of the \mathcal{T}_d group. With this change of basis we obtain the decomposition $A_1 \oplus F_2$ for the stretches and $A_1 \oplus E \oplus F_2$ for the bends. From this result we readily identify the A_1 bending mode as the spurious state. We now eliminate this spurious state from the space and proceed to construct the higher phonon basis from the physical one-phonon set by means of the coupling coefficients $C(;)$

$${}^{V_1+V_2}\Psi_{\gamma}^{\Gamma} = \sum_{\gamma_1 \gamma_2} C(\Gamma_1 \Gamma_2 \Gamma; \gamma_1 \gamma_2 \gamma) {}^{V_1}\Psi_{\gamma_1}^{\Gamma_1} {}^{V_2}\Psi_{\gamma_2}^{\Gamma_2} , \quad (3)$$

where Γ and γ label the irreps of \mathcal{T}_d and its components, respectively.

To eliminate the spurious contributions from the Hamiltonian we demand its null expectation value with respect to the one-phonon spurious functions [7]

$$\langle {}^1\Psi_{\text{bending}}^{A_1} | \hat{\mathcal{H}} | {}^1\Psi_{\text{bending}}^{A_1} \rangle = 0 , \quad (4)$$

which leads to a constraint

$$4(1 - N_2)A_5 + 16(1 - 2N_2)B_{5,6} + 4(1 - 2N_2)B_{5,10} = 0$$

between the interaction parameters.

The vibrational energies are obtained by diagonalizing the Hamiltonian (1) with respect to the normal basis (3), constructed from the projected one-phonon functions (A_1, F_2)–stretching and (E, F_2)– bending, taking into account the constraint (4).

TABLE I. Experimental [2,6,9] and calculated energies (cm^{-1}) for methane.

| V | Normal label | Γ | Expt. | Calc. | V | Normal label | Γ | Expt. | Calc. |
|---|------------------|----------|--------|--------|-------------------------|-------------------------|----------|--------|--------|
| 1 | ν_4 | F_2 | 1310.0 | 1303.7 | 3 | $\nu_1 + \nu_2 + \nu_4$ | F_1 | 5775.0 | 5745.6 |
| | ν_2 | E | 1533.0 | 1520.4 | | | F_2 | | 5759.9 |
| | ν_1 | A_1 | 2916.5 | 2918.4 | | | A_2 | | 5854.4 |
| | ν_3 | F_2 | 3019.4 | 3027.2 | | | E | | 5854.4 |
| 2 | $2\nu_4$ | A_1 | | 2474.5 | | $\nu_2 + \nu_3 + \nu_4$ | F_1 | | 5854.4 |
| | | E | | 2476.4 | | | F_2 | 5854.4 | |
| | | F_2 | 2614.0 | 2610.5 | | | A_1 | 5868.7 | |
| | $\nu_2 + \nu_4$ | F_1 | | 2827.2 | | | E | 5868.7 | |
| | | F_2 | 2830.4 | 2841.5 | | | F_1 | 5868.7 | |
| | $2\nu_2$ | A_1 | | 3003.7 | | | F_2 | 5861.0 | 5868.7 |
| | | E | | 3026.3 | | $\nu_1 + 2\nu_2$ | A_1 | | 5922.0 |
| | $\nu_1 + \nu_4$ | F_2 | 4223.0 | 4222.0 | | | E | 5944.7 | |
| | $\nu_3 + \nu_4$ | A_1 | | 4330.9 | $2\nu_2 + \nu_3$ | F_2 | | 6030.9 | |
| | | E | | 4330.9 | | F_1 | 6053.5 | | |
| | | F_1 | | 4330.9 | F_2 | 6053.5 | | | |
| | $\nu_2 + \nu_3$ | F_2 | 4319.0 | 4330.9 | $2\nu_1 + \nu_4$ | F_2 | | 7091.7 | |
| | | F_1 | | 4547.7 | $\nu_1 + \nu_3 + \nu_4$ | A_1 | | 7160.4 | |
| | F_2 | 4549.0 | 4547.7 | E | | 7160.4 | | | |
| | $\nu_1 + \nu_2$ | E | | 4438.8 | | F_1 | 7160.4 | | |
| | $2\nu_1$ | A_1 | | 5788.0 | | F_2 | 7160.4 | | |
| | $\nu_1 + \nu_3$ | F_2 | 5861.0 | 5856.7 | $2\nu_3 + \nu_4$ | F_2 | | 7278.1 | |
| | $2\nu_3$ | A_1 | | 5974.4 | | E | 7308.4 | | |
| | | F_2 | 6004.7 | 6014.5 | | A_1 | 7318.2 | | |
| | | E | | 6047.7 | F_1 | 7318.2 | | | |
| 3 | $3\nu_4$ | F_2 | | 3624.3 | $2\nu_1 + \nu_2$ | F_2 | | 7318.2 | |
| | | F_1 | | 3778.3 | | F_2 | 7351.4 | | |
| | | F_2 | | 3779.4 | | F_1 | 7351.4 | | |
| | A_1 | | 3920.4 | E | | 7318.2 | | | |
| | $\nu_2 + 2\nu_4$ | A_1 | | 3925.7 | $\nu_1 + \nu_2 + \nu_3$ | F_1 | | 7377.1 | |
| | | E | | 3935.6 | | F_2 | 7377.1 | | |
| | | E | | 3987.9 | $\nu_2 + 2\nu_3$ | E | | 7494.8 | |
| | | A_2 | | 4017.6 | | F_1 | 7534.9 | | |
| | | F_2 | 4123.0 | 4123.9 | | F_2 | 7514.0 | 7534.9 | |
| | | F_1 | | 4260.4 | | E | 7568.1 | | |
| | $2\nu_2 + \nu_4$ | F_1 | | 4425.5 | A_2 | | 7568.1 | | |
| | | F_2 | | 4317.4 | A_1 | | 7568.1 | | |
| | | F_2 | | 4387.6 | $3\nu_1$ | A_1 | | 8581.1 | |

| V | Normal label | Γ | Expt. | Calc. | V | Normal label | Γ | Expt. | Calc. |
|---|------------------|----------|--------|--------|-------|------------------|------------------|--------|--------|
| | $3\nu_2$ | A_1 | | 4495.3 | | $2\nu_1 + \nu_3$ | F_2 | 8604.0 | 8603.0 |
| | | E | | 4510.9 | | | $\nu_1 + 2\nu_3$ | A_1 | |
| | | A_2 | | 4575.7 | | F_2 | | 8807 | 8794.1 |
| | $\nu_1 + 2\nu_4$ | A_1 | | 5392.8 | | E | | | 8838.5 |
| | | E | | 5394.7 | | $3\nu_3$ | F_2 | 8900.0 | 8910.0 |
| | | F_2 | | 5501.7 | | | F_1 | | 8944.8 |
| | F_1 | | 5503.6 | | A_1 | | | 8982.1 | |
| | $\nu_3 + 2\nu_4$ | F_2 | | 5503.6 | | F_2 | 9045.0 | 9034.5 | |
| | | F_2 | | 5528.8 | | | | | |
| | | F_2 | | 5637.7 | | | | | |
| | | A_1 | | 5637.7 | | | | | |
| | | E | | 5637.7 | | | | | |
| | | F_1 | | 5637.7 | | | | | |

3 Methane

In this section we apply this algebraic approach to describe the vibrational levels of methane. According to the Hamiltonian (1) the number of parameters is eight, plus the boson numbers N_1 and N_2 . The vibron number N_1 can be fixed from the anharmonicity of the $C - H$ bond, while for the bending vibrations we have taken N_2 from the $H - H$ interaction in H_2O given in reference [8]. From these considerations, the number of free parameters is seven, taking into account the constraint (4).

TABLE II. Parameters of the Hamiltonian obtained in the least square fitting (cm^{-1}). The numbers of bosons are taken to be $N_1=43$ and $N_2=28$.

| Stretching | | | Bending | | | | | rms |
|------------|----------|----------------|---------|-----------|------------|-----------------|------------------|-------|
| A_1 | B_{12} | λ_{12} | A_5 | $B_{5,6}$ | $B_{5,10}$ | $\lambda_{5,6}$ | $\lambda_{5,10}$ | |
| -13.2125 | -0.6850 | 0.6328 | 35.4844 | 2.6492 | -28.0164 | 9.0501 | 5.1799 | 12.16 |

The Hamiltonian (1) is diagonalized in the normal basis, built by repeated couplings of the form (3). Since by construction this basis is symmetry adapted, the Hamiltonian matrix separates into blocks corresponding to the irreps of T_d . In Table I we present the least square fit for methane up to three quanta. Following Herzberg's notation [6], the four fundamental energies for A_1 , F_2 (stretching) and E , F_2 (bending) have been denoted by ν_1 , ν_3 , ν_2 and ν_4 , respectively. The final parameters are given in Table II. The model in its simplest form (without

including the V^{B-S} interaction or higher order terms) seems to provide a good description of 19 experimental energy levels with an *rms* deviation of 12.16 cm^{-1} .

4 Conclusions

We have presented a new method, which applied to an algebraic model of coupled anharmonic oscillators is able to describe the complete vibrational spectrum of polyatomic molecules. We emphasize that the method systematically incorporates group theoretical techniques which simplify the diagonalization of the Hamiltonian and provide a clear methodological procedure that can be applied to other molecules [10]. Although we have used the model in its simplest form, it can be improved in the following ways: a) Inclusion of the stretching-bending interactions \hat{V}^{S-B} , (b) Introduction in the Hamiltonian of higher order terms and (c) Addition of interactions which do not conserve the total number of quanta.

Acknowledgments

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